An exponentiated DWBA formula for H-atom transfers. Extensions to lower barrier potentials and to higher energies

Vasil K. Babamov
Department of Chemistry, California State University-Long Beach, Long Beach, California 94840 and Centro de Graduados, Instituto Tecnologico de Tijuana, Apdo Postal 1166, Tijuana, B. C., Mexico

Vicente Lopez[a] and R. A. Marcus[b]
Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

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Analytic formulas obtained earlier for the probability of H-atom transfer between two heavy particles in the threshold region are extended to higher energies and to systems with lower barrier potentials. The calculated reaction probability vs energy curve is in good agreement with numerical results for the model system investigated involving transfer between two nearly degenerate states.

I. INTRODUCTION

The dynamics of a light atom transfer between two nearly degenerate vibrational states in a collinear A + HB→AH + B collision, where H denotes the light atom, has been studied recently.[1-7] It was shown[1-3] that the reaction dynamics can be represented approximately in terms of the two nearly degenerate vibrational states, suitably distorted throughout the collision, between which the exchange occurs. Approximate solution of the resulting two coupled equations yielded analytical formulas for the reactive transition probability in the threshold region.[1,2] They were tested in Ref. 2 for reactions which have a nonnegligible activation energy.

In this paper we present approximate analytical formulas for the transition probability valid at higher energies up to the limit of validity of the two-state approximation. The formulas are also valid for reactions with a smaller barrier height (a small activation energy) for which the treatment in Ref. 2 is not applicable.

The procedure for calculating the potential energy matrix in a set of two coupled equations in the diabatic representation, on which the treatment is based, is given in Sec. II. The approximate analytical formulas are presented and tested against an accurate numerical solution of the two-state coupled equations in Sec. III. A discussion of the results and their relation to alternative treatments is given in Sec. IV.

II. EVALUATION OF THE EFFECTIVE EXCHANGE COUPLING

It was shown earlier[1-3] that in a collinear H atom transfer collision in which one of the product states is nearly degenerate with the initial reactant one the dynamics of the collision can be approximately represented by two coupled equations which correspond to the two nearly degenerate states between which the exchange occurs.

A set of coupled equations in the adiabatic representation can be constructed[8] by expanding the wave function of the system in terms of the local eigenfunctions $\chi(s;\rho)$ of the double minimum potential $V(s,\rho)$[1,2]:

$$\psi = \sum_j \varphi_j(\rho)\chi_j(s;\rho), \tag{2.1}$$

where s is an arc length $\rho\vartheta$ in a mass-weighted internal coordinate space for the collinear triatomic system and ρ and ϑ are polar coordinates. χ_j depends on s and parametrically on ρ. On substituting the expansion into the Schrödinger equation in polar coordinates and integrating over the ϑ dependence one obtains the coupled equations[1,4]

$$\left[-\frac{1}{2}\frac{d^2}{d\rho^2} - \left(E - \epsilon_i + \frac{1}{8\rho^2}\right)\right]\varphi_i(\rho) + \sum_j \left(-iA_{ij}\frac{d}{d\rho} + \frac{1}{2}Q_{ij}\right)\varphi_j(\rho) = 0. \tag{2.2}$$

The notation is that of Refs. 1 and 4 with A replacing P.

A pair of coupled equations which involves only the two nearly degenerate states can readily be obtained by truncating Eq. (2.2) to obtain

$$\left[-\frac{1}{2}\frac{d^2}{d\rho^2} + \epsilon_i(\rho) - E + Q_{ii}\right]\varphi_i(\rho) = iA_{ij}\frac{d}{d\rho}\varphi_j(\rho), \tag{2.3}$$

$$\left[-\frac{1}{2}\frac{d^2}{d\rho^2} + \epsilon_j(\rho) - E + Q_{jj}\right]\varphi_j(\rho) = iA_{ji}\frac{d}{d\rho}\varphi_i(\rho),$$

where the negligible $1/8\rho^2$ term has been omitted for simplicity. Solving Eq. (2.3) directly (e.g., Ref. 8) may lead to inaccuracies, since the adiabatic coupling elements A_{ij} contain other contributions[9] aside from the exchange interaction (similar to the "translational factor" in gas phase electron transfers[10]). One can construct[1] another pair of coupled equations in the diabatic representation in which the coupling represents only the exchange interaction[9], namely

$$\left[-\frac{1}{2}\frac{d^2}{d\rho^2} + V_{ii}(\rho) - E\right]\Psi_i(\rho) = V_{ij}\Psi_j(\rho), \tag{2.4}$$

$$\left[-\frac{1}{2}\frac{d^2}{d\rho^2} + V_{jj}(\rho) - E\right]\Psi_j(\rho) = V_{ji}\Psi_i(\rho).$$

[a] Permanent Address: Departamento de Quimica Fisica y Quimica Cuantica, Universidad Autonoma de Madrid Cantoblanco, Madrid-34, Spain.
[b] Contribution No. 6924.

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The potential matrix elements V_{ij} were evaluated in Refs. 1 and 2 for the threshold region of reaction, with the aid of the diagonal potential matrix elements of Eq. (2.3): Two methods were described in Refs. 1 and 2 for determining the diabatic states from the adiabatic states. A more general method which covers a broader range of conditions is described below. At the energies used in Refs. 1 and 2 it gives results in excellent agreement with the ones obtained from the other methods, but, in addition, is applicable to higher energies and to lower barriers. The three methods are compared in Sec. IV.

Localized (diabatic) vibrational states $\zeta(s;\rho)$ can be defined at every ρ as that linear combination of the two adiabatic states $\chi(s;\rho)$ for which the H atom is localized near the atom A or B. The most localized diabatic states ζ_i and ζ_j, elements of a column vector $\boldsymbol{\zeta}(s;\rho)$, can be found by finding a suitable orthogonal transformation matrix $\mathbf{T}$ which acts on the column vector $\boldsymbol{\chi}(s;\rho)$ with elements χ_i and χ_j:

$$\boldsymbol{\zeta}(s;\rho) = \mathbf{T}\boldsymbol{\chi}(s;\rho) \tag{2.5}$$

[cf. Eq. (3.3) in Ref. 1]. We consider potentials such that in the domain of ρ's important for the reaction, the potential for a given ρ has two distinct wells as a function of s. For these double minimum potentials the most localized wave functions ζ_i and ζ_j will be construed as the ones for which the probability density within one well of the potential is the highest.[11]

The transformation matrix $\mathbf{T}$ can then be used to transform the diagonal potential energy matrix $\boldsymbol{\epsilon}$ in Eq. (2.3) into the desired diabatic potential energy matrix $\mathbf{V}$ in Eq. (2.4).[12]

$$\mathbf{V} = \mathbf{T}\boldsymbol{\epsilon}\,\tilde{\mathbf{T}}. \tag{2.6}$$

The above procedure gives results for reaction probabilities which are in excellent agreement with the ones obtained using the alternative procedures in Ref. 1 at the energies for which the latter can be evaluated.

The diagonal potential matrix elements obtained as above for the two lowest pairs of nearly degenerate states in the model BrH + Cl→Br + HCl system studied in Refs. 1–3 are shown in Fig. 1 (solid curves). Shown in Fig. 2 is the logarithm of the interaction matrix element V_{ij} obtained as above for these two pairs of states.

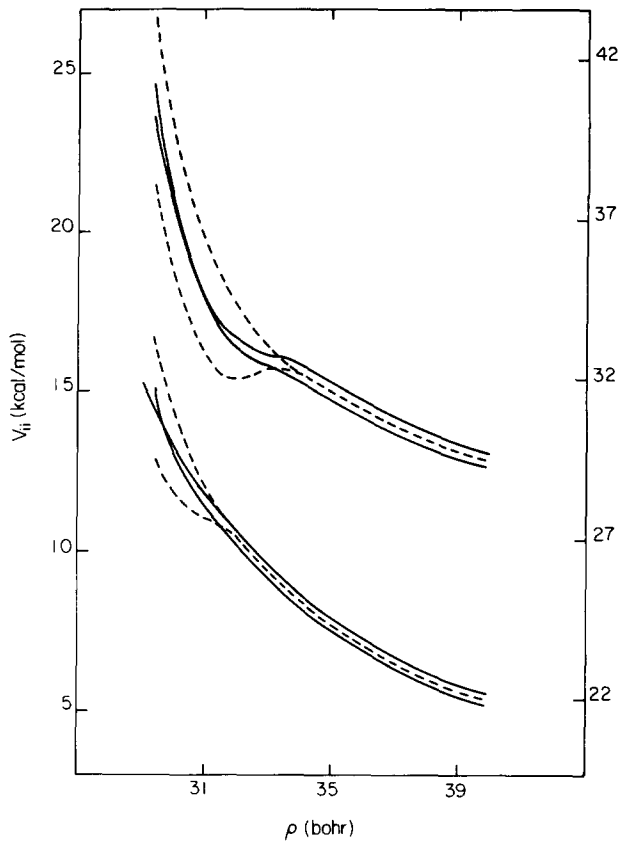

FIG. 1. Plot of diabatic eigenvalues $V_{ii}(\rho)$ (solid curves) vs ρ for the states which correspond asymptotically to Cl + HBr ($v = 0$), ClH($v = 2$) + Br, Cl + HBr($v = 1$), ClH($v = 3$) + Br, in order of increasing energy. The dashed curves are the adiabatic eigenvalues of a corresponding degenerate problem, obtained from the V_{ii} and V_{ij} as described in Eqs. (4) and (5) of Ref. 2. The numbers on the left- (right-) hand side are relative to the minimum of the HBr (HCl) well.

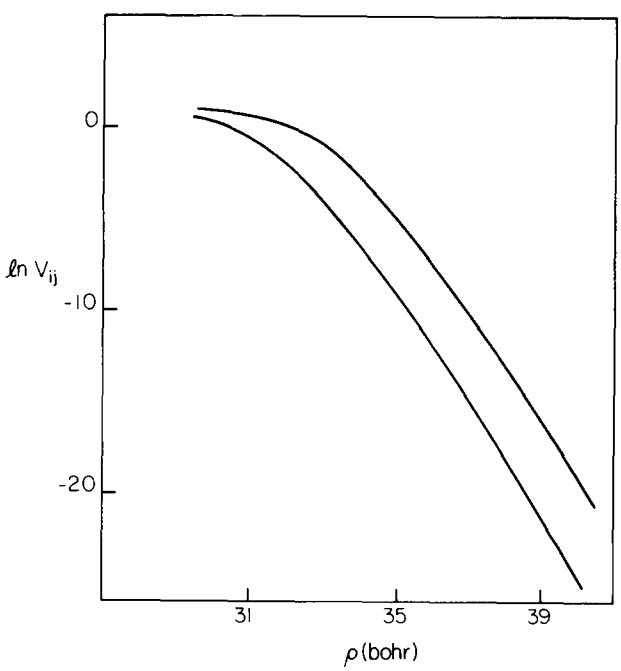

FIG. 2. Plot of ln $V_{ij}(\rho)$ vs ρ for the lowest pair of nearly degenerate states (lower curve) and for the next pair of states (upper curve) for the system in Fig. 1.

III. MODIFICATIONS OF THE EXPONENTIATED DWBA FORMULA FOR LOWER BARRIER POTENTIALS AND/OR HIGHER ENERGIES

The DWBA approximation to the transition probability for the nearly degenerate H-atom transfer problem represented by Eq. (2.4) can be written in terms of an integral[1] T^0_{ij}.

$$T^0_{ij} = \int \psi^0_i(\rho) V_{ij}(\rho) \psi^0_j(\rho) d\rho, \tag{3.1}$$

where the $\psi^0_k(\rho)$ are the real solutions, regular at small ρ, of Eq. (2.4) with the right-hand side set to zero, i.e., of

$$\left[-\frac{1}{2}\frac{d^2}{d\rho^2} + V_{kk}(\rho) - E \right] \psi^0_k(\rho) = 0, \quad (k = i,j). \tag{3.2}$$

It was shown in Ref. 2 that the DWBA transition probability P_{ij} for a nearly degenerate H-atom transfer $[= (2\pi T^0_{ij})^2]$

can be written in terms of the DWBA transition probability $P^D_{\rm sym}$ for a corresponding degenerate H-atom transfer problem, as in Eq. (3a) in Ref. 2:

$$P_{ij} = (2\pi T^0_{ij})^2 = [e^{-\Delta^2/2\alpha F}]^2 P^D_{\rm sym}, \tag{3.3}$$

where Δ is the resonance defect $V_{ii}(\rho) - V_{jj}(\rho)$ evaluated at the classical turning point ρ_0, F is $(dV^0_{ii}/d\rho)_{\rho_0}$, $V^0_{ii}(\rho)$ being $1/2\,[V_{ii}(\rho) + V_{jj}(\rho)]$, and α is $-[d \ln V_{ij}(\rho)/d\rho]_{\rho_0}$ This corresponding degenerate H-atom transfer problem is defined by Eqs. (4) and (5) of Ref. 2.

The above simple DWBA formula, derived by linearizing V_{ii} and $\ln V_{ij}$ in Eq. (2.4) as a function of ρ and by taking $V_{ii} - V_{jj}$ as constant, can become inaccurate at energies high above the reaction threshold. As shown in Ref. 2 such deviations at higher energies do not influence significantly its utility for evaluating reaction rates at low to moderate temperatures, since the latter depend mainly on the behavior of P_{ij} in the threshold region. However, the DWBA formula (3.3) also becomes inaccurate for potentials with saddle-point barrier heights of only a few kcal/mol or less, since for such reactions the V^0_{ii} vs ρ plot can deviate strongly from linearity. The latter plot may even have a well as a function of ρ, which leads to quasibound states or "resonances" in the strong interaction region. The method given below handles this latter source of difficulty, and also treats the case where there are deviations of the energy defect $V_{ii}(\rho) - V_{jj}(\rho)$ from constancy and of $V^0_{ii}(\rho)$ and $\ln V_{ij}(\rho)$ from linearity.

When the resonance defect $V_{ii} - V_{jj}$ is nearly constant and the potential matrix element V^0_{ii} and $\ln V_{ij}$ are nearly linear as a function of ρ throughout the interaction region, the DWBA result Eq. (2.3) can readily be extended to higher energies simply by replacing $P^D_{\rm sym}$ in Eq. (3.3) by the exact two-state result[2] for the corresponding degenerate exchange problem. Denoting this new quantity by $P_{\rm sym}$, we have[2]

$$P_{\rm sym} = \sin^2(\xi^s_0 - \xi^\alpha_0), \tag{3.4}$$

where ξ^s_0 and ξ^α_0 are the elastic phase shifts for the ρ motion on the hypothetical symmetric and antisymmetric adiabatic eigenvalue curves defined by Eqs. (4) and (5) of Ref. 2. The latter are depicted in the present Fig. 1 as the dashed curves.

The resonance defect $V_{ii}(\rho) - V_{jj}(\rho)$ is often not constant and $V^0_{ii}(\rho)$ and $\ln V_{ij}$ are often not linear as a function of ρ. An improved approximation for the transition probability P_{ij} can be obtained by averaging the influence of the resonance defect over the effective interaction strength $f(\rho)$ during the collision, e.g., by replacing Eqs. (3.3) and (3.4) by

$$P_{ij} \approx \langle e^{-\Delta^2/2\alpha F}\rangle^2 \sin^2(\xi^s_0 - \xi^\alpha_0), \tag{3.5}$$

where

$$\langle e^{-\Delta^2/2\alpha F}\rangle = \frac{\int_{\rho_0}^{\infty} f(\rho)\exp\{-\Delta^2(\rho)/2\alpha(\rho)F(\rho)\}d\rho}{\int_{\rho_0}^{\infty} f(\rho)d\rho}. \tag{3.6}$$

Here $\Delta(\rho)$, $\alpha(\rho)$, and $F(\rho)$ now denote $V_{ii}(\rho) - V_{jj}(\rho)$, $-d \ln V_{ij}(\rho)/d\rho$, and $dV^0_{ii}(\rho)/d\rho$, respectively. The weighting function $f(\rho)$ in Eq. (3.6) is taken to be the integrand in an approximate semiclassical perturbation expression for $2\pi T^0_{12}$, namely in[13]

$$2\pi T^{0sc}_{12} = 2\int_{\rho_0}^{\infty} V_{12}d\rho/p_0(\rho), \tag{3.7}$$

where $p_0(\rho)$ equals $\{2[E - V^0_{ii}(\rho)]\}^{1/2}$. Thus, we have

$$f(\rho) = \frac{V_{12}(\rho)}{\{2[E - V^0_{ii}(\rho)]\}^{1/2}}. \tag{3.8}$$

A comparison of the results of Eqs. (3.5)–(3.8) with results of an accurate numerical solution of Eq. (2.4) is shown in Fig. 3 for the lowest two pairs of nearly degenerate states of the model system of Refs. 1–3.

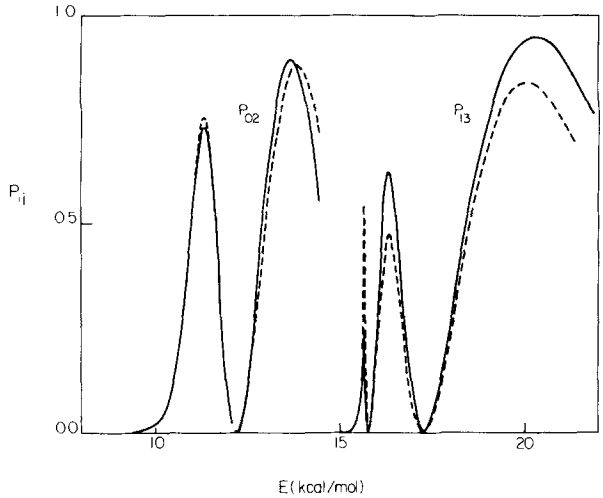

FIG. 3. Reaction probabilities P_{02} and P_{13} vs total energy E relative to minimum of HBr potential. The dashed curves are those given by Eq. (3.4). The solid curves represent the numerical solution of the two-state problem.[3]

IV. DISCUSSION

The results of the analytical extension of the DWBA formulas for a nearly degenerate H-atom transfer to higher energies presented here are seen from Fig. 3 to be in very good agreement with the results of the numerical solutions of the two-state problem, Eq. (2.4). Previously, the numerical solution of Eq. (2.4) had itself been shown to agree well with accurate multichannel results for the same system.[3] The deviation of the present results of Eq. (3.7) from those obtained by solving Eq. (2.4) numerically is comparable to the deviation of the latter from the accurate multichannel ones.[3]

We consider next the various maxima in Fig. 3. The first sharp peak in the P_{13} curve (at about 15.65 kcal/mol) in Fig. 3 is a resonance,[3] as one can indeed anticipate from the well in the adiabatic eigenvalue which corresponds mainly to the $v = 3$ state of HCl (cf. Fig. 4 of Ref. 3, and also the corresponding dashed curve in the present Fig. 1, the second from the top.) The next P_{13} maximum occurs at an energy where the $1 \rightarrow 3$ reaction becomes classically allowed for such adiabatic states, namely,at an energy where the mean of the adiabatic eigenvalues at the turning-point ρ_0 approximates the local maximum of the double well potential $V(s,\rho)$ at ρ_0.[14] The first P_{02} peak occurs at an energy (11.3 kcal/mol) somewhat less than that (11.75 kcal/mol) where the $0 \rightarrow 2$ reaction becomes classically allowed for these adiabatic states. Presumably it occurs at that low energy because of very extensive

H-atom tunneling.

The problem of solving Eq. (2.4) is also encountered in treating the transfer of an electron between two atoms and is known as the Demkov problem[15] in the atomic physics literature. Approximate solutions to Eq. (2.4) valid at energies high above, but not near or below the threshold have been devised.[15–17]

In concluding this section we consider the factor multiplying $P_{\rm sym}$ in Eqs. (3.3) and also the choice of diabatic states.

The factor multiplying $P_{\rm sym}$ in the DWBA Eq. (3.3) has an interesting interpretation. We first note that in the vicinity of the classical turning-point ρ_0 of the ρ motion, the integration of the ρ equations [Eqs. (4.11) and (5.2) of Ref. 1] yields $(\rho-\rho_0)^{1/2}=(F/2)^{1/2}\tau$, where τ is the time for the system to go from ρ_0 to ρ. We consider next the relevant value of $\rho-\rho_0$ for change of V_{ij}^2 with ρ. (In the simple DWBA model, the reaction probability is proportional to V_{ij}^2.) V_{ij}^2 decreases to $1/e$th of its value at ρ_0 when $\rho-\rho_0$ equals $1/2\alpha$. The total time spent by the system in this $\rho-\rho_0$ interval is of the order of τ (really 2τ) equal to $[2(\rho-\rho_0)/F]^{-1/2}$, i.e., $(\alpha F)^{-1/2}$. Remembering that the results are in units of $\hbar=1$, one sees that the presence of the $\exp[-\Delta/(\alpha F)^{1/2}]^2$ factor in Eq. (3.3) reflects the Heisenberg uncertainty principle.

This factor serves as the counterpart to the well-known delta function $\delta(\Delta)$ which appears in Golden Rule expressions for radiationless transitions and for electron transfer reactions. Because the mass ratio in H transfers (ratio of mass of light particle to the heavier masses) is smaller than in electron transfers, the $\delta(\Delta)$ factor is replaced by a less severe constraint, namely the $\exp[-(\tau\Delta)^2]$ factor. This factor also has as its counterpart an analogous factor such as $\mathrm{sech}^2\tau\Delta$, obtained from a classical path treatment of a glancing atomic collision in charge transfer processes,[15–17] τ being a rough measure now of the "collison time" for such collisions.

We have given previously[1] two alternative ways of calculating the diabatic states at each value of ρ: in one of these the diabatic states were calculated from the adiabatic ones via approximate relations connecting the two.[1] A second way was to use the same method to determine the diagonal elements V_{ii} and V_{jj}, but to use a semiclassical method to determine the off-diagonal element V_{ij} in terms of a tunneling integral between the two wells.[1] This second method provided a more accurate determination of the off-diagonal element V_{ij} when V_{ij} was small but, unlike the first, was restricted to the case where each of the separated wells were deep enough to individually support at least one quantum state at the desired range of ρ. As such it was limited to energies below the classical reaction threshold, i.e., to the purely tunneling region of the dynamics.

The present method for obtaining the diabatic states of each ρ from the adiabatic ones is as easily applied as the other two. Unlike the second it does not require each of the wells to support a quantum state and unlike the first it is still accurate at small V_{ij}. Thus, it has virtues of both previous methods. In the energy range where those two methods were applied[1,2] all three methods give similar results for the transition probability, P_{ij} and, indeed, the present method is the one employed in Ref. 2, as already noted there. An advantage, nevertheless, of the semiclassical method given in Ref. 1 over the other two methods is that it can be used for extremely small V_{ij}'s.

ACKNOWLEDGMENTS

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[9] In particular, a vibrational wavefunction localized on the products appears to change with ρ, when expressed in terms of coordinates (s,ρ) or (θ,ρ) even when it would not change if expressed in terms of the product's own internal coordinate. This kind of dependence of $\chi_i(s;\rho)$ on ρ is reflected in the adiabatic coupling elements A_{ij} in Eq. (2.3). Using Eq. (2.4) instead of Eq. (2.3) ensures that this misleading contribution to the A_{ij}'s does not affect the transition probabilities. In the corresponding problem with two degenerate states, i.e., the one described by the dashed lines later in Fig. 1, the coupling terms A_{ij} vanish identically (cf. Sec. IV of Ref. 4) and so the above "translational" effect does not influence the $P_{\rm sym}$ appearing in Eqs. (3.3) or (3.4) and hence does not influence the P_{ij} calculated from those equations.
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[11] Let $\mathbf{T}$ be an orthogonal matrix with elements $T_{ii}=T_{jj}=\cos\varphi$, $T_{ij}=-T_{ji}=\sin\varphi$. We chose φ at each ρ so that the function ζ_i (of the pair ζ_i,ζ_j) in Eq. (2.5) maximizes the value of $\int_0^{s^b}\zeta_i^2(s;\rho)ds$, where $s^b(\rho)$ is the value of s at the local maximum of the double-well potential at any ρ. This method applies, of course, to ρ's where this potential has indeed a local maximum separating the reactants' from the products' region.
[12] We note that the elements of $\mathbf{V}$ are $V_{ij}=\langle\zeta_i|H_s|\zeta_j\rangle$ and those of $\boldsymbol{\epsilon}$ are $\epsilon_{ij}=\langle\chi_i|H_s|\chi_j\rangle$, where $H_s=-\frac{1}{2}\partial^2/\partial s^2+V(s,\rho)$. The χ's diagonalize H_s [as in Eq. (3.4) of Ref. 4].
[13] See Eqs. (4.10) and (5.7) of Ref. 4, noting that $\epsilon^a-\epsilon^s=2V_{ij}(\rho)$, as one sees from Eq. (3.7b) of Ref. 1. A probably more accurate but also more laborious alternative is to use the integrand of the present Eq. (3.1) for $f(\rho)$ and

integrate (3.6) from 0 to ∞.

[14]We note that the mean of these two eigenvalues approximates the eigenvalue of a single well [to see this one can apply Eq. (5.1) of Ref. 4], and so here the latter approximates the barrier maximum.

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